

DESIGN OF TRANSITION-METAL OSCILLATORS BASED ON THE REDUCTION OF PERMANGANATE IONS BY KETO DICARBOXYLIC ACIDS

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Permanganate chemical oscillators with some keto dicarboxylic acids in the presence of phosphoric acid in a continuously stirred tank reactor (CSTR) are described in terms of the phase diagrams in the [ketomalonic acid]_o-k_o, [oxalacetic acid]_o-k_o, and [α -ketoglutaric acid]_o-k_o planes, and in the [H₃PO₄]_o-k_o, [MnO₄]_o-k_o, temperature-k_o planes. The results show that an optimum degree of stabilization of the Mn(IV) colloid, which may serve as a reservoir of solvated Mn(IV) ions participating in the elementary reaction steps, is a prerequisite for the oscillations in the MnO₄⁻-keto dicarboxylic acid system. A skeleton mechanism for permanganate oscillators with keto dicarboxylic acids involving five reaction steps is proposed.

Previously we described permanganate chemical oscillators based on the oxidation of keto dicarboxylic acids, i.e. ketomalonic, oxalacetic and α -ketoglutaric acids, by MnO₄⁻ ions¹. We feel that a more detailed study into this subgroup of permanganate oscillators may provide a new insight into their reaction mechanism. The aim of this work was to design oscillating systems based on the reduction of MnO₄⁻ ions by ketomalonic, oxalacetic and α -ketoglutaric acid in a continuous stirred tank reactor (CSTR), which may be interesting also from the point of view of transition metal chemistry.

EXPERIMENTAL

A glass CSTR (ref.²) 27.6 cm³ whose jacket was connected to a TB 150 ultrathermostat (Medingen) was used. The oscillatory reactions in a flowing, well-stirred solution were monitored voltamperometrically by means of an LP7 polarograph (Laboratorni pristroje, Prague, The Czech Republic) equipped with a static platinum electrode. The stirring frequency in the reactor was 2 250 min⁻¹. The experimental procedure was as in our earlier work³.

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RESULTS AND DISCUSSION

In our previous work dealing with permanganate chemical oscillators⁴⁻⁹, a solution of phosphoric acid was always used as the reaction medium with regard to its ability to stabilize colloidal MnO_2 . Only in the presence of phosphoric acid we were able to observe oscillatory behaviour of permanganate oxidations of keto dicarboxylic acids. For example, the influence of the concentration of H_3PO_4 on the dynamic behaviour of the permanganate oscillator with ketomalonic acid in CSTR was studied over the concentration range of $1 \cdot 10^{-4} \text{ mol dm}^{-3}$ to $16 \cdot 10^{-4} \text{ mol dm}^{-3}$. As Fig. 1 demonstrates, sustained oscillations only occur within a very narrow range of H_3PO_4 concentrations and of k_0 values. Kinetic bistability between sustained oscillations and the oxidized steady state (OSS) occupies a slightly broader H_3PO_4 concentration range. It is interesting that kinetic bistability between the oxidized and reduced steady states (OSS and RSS) has already been observed for the H_3PO_4 concentration region from $1 \cdot 10^{-4} \text{ mol dm}^{-3}$ to $4 \cdot 10^{-4} \text{ mol dm}^{-3}$. In that case we have apparently found an oscillatory state within the frame of the "cross phase diagram"^{10,11}.

The phase diagrams of the permanganate oscillator with oxalacetic acid exhibit more pronounced regions of sustained oscillations which are adjacent to a dynamic state of damped oscillations (Fig. 2). The relatively wide region of damped oscillations in the neighbourhood of the region of sustained oscillations suggests a Hopf bifurcation on the borderline separating the two regions. Fortunately, there is a fairly broad region of well-reproducible sustained oscillations that are not disturbed by precipitation of

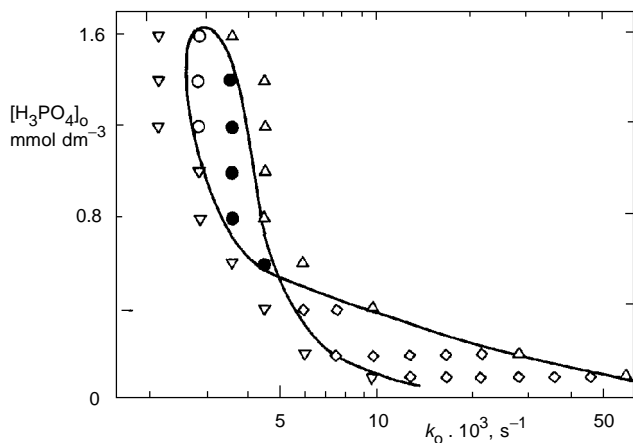


FIG. 1

Phase diagram for the MnO_4^- -ketomalonic acid system in the $[\text{H}_3\text{PO}_4]_0$ - k_0 plane. $[\text{KMnO}_4]_0 = 0.01 \text{ mmol dm}^{-3}$, $[\text{ketomalonic acid}]_0 = 0.016 \text{ mmol dm}^{-3}$, temperature $30 \text{ }^\circ\text{C}$, k_0 is the flow rate in s^{-1} ; ∇ reduced steady state, Δ oxidized steady state, \circ oscillatory state, \diamond bistability of OSS and RSS, \bullet bistability of OSS and oscillations

FIG. 2
Phase diagrams for the MnO_4^- -oxalacetic acid (OAA) system in the planes: *a* $[\text{KMnO}_4]_0$ - k_0 , *b* $[\text{H}_3\text{PO}_4]_0$ - k_0 , *c* $[\text{OAA}]_0$ - k_0 . Fixed constraints: *a* $[\text{OAA}]_0 = 0.125 \text{ mmol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 1 \text{ mmol dm}^{-3}$; *b* $[\text{KMnO}_4]_0 = 0.05 \text{ mmol dm}^{-3}$, $[\text{OAA}]_0 = 0.125 \text{ mmol dm}^{-3}$; *c* $[\text{KMnO}_4]_0 = 0.05 \text{ mmol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 1 \text{ mmol dm}^{-3}$; temperature 20°C . \square Steady state, Δ oxidized steady state, \circ sustained oscillations, \bullet damped oscillations

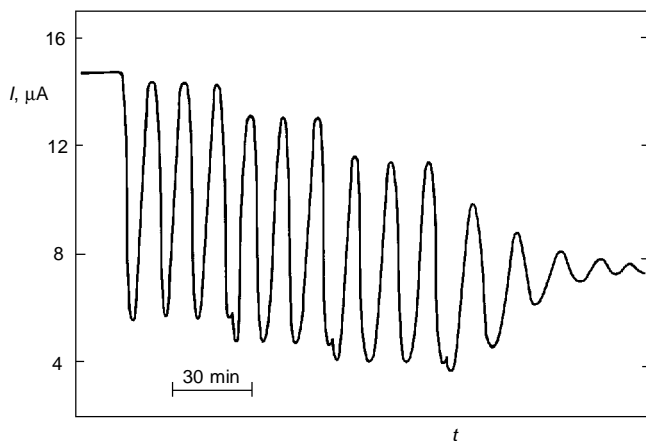
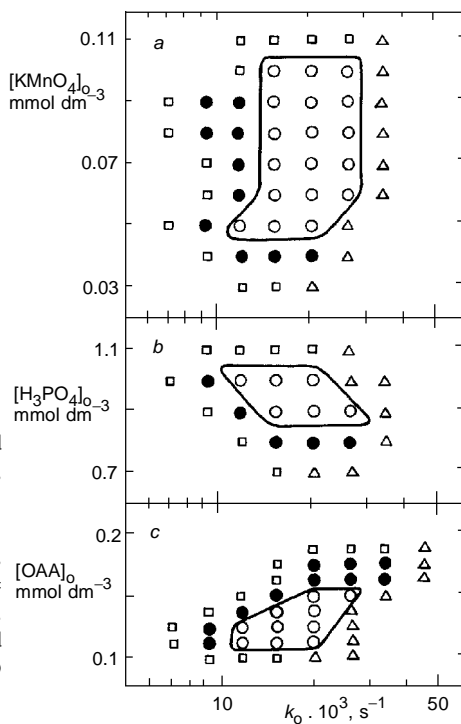


FIG. 3
Sustained and damped oscillations of the MnO_4^- -oxalacetic acid (OAA) system. Fixed constraints: $[\text{KMnO}_4]_0 = 0.05 \text{ mmol dm}^{-3}$, $[\text{OAA}]_0 = 1.25 \text{ mmol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 1 \text{ mmol dm}^{-3}$, temperature 20°C

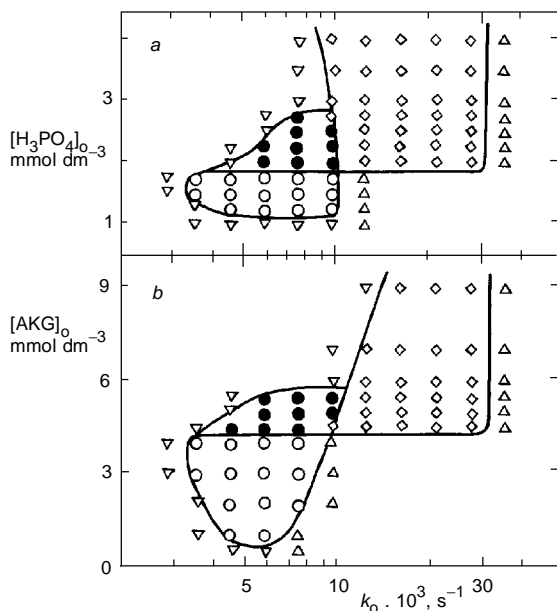


FIG. 4

Phase diagrams of the MnO_4^- - α -ketoglutaric acid (AKG) system in the planes: *a* $[\text{H}_3\text{PO}_4]_0$ - k_0 , *b* $[\text{AKG}]_0$ - k_0 . Fixed constraints: *a* $[\text{KMnO}_4]_0 = 0.08 \text{ mmol dm}^{-3}$, $[\text{AKG}]_0 = 0.5 \text{ mmol dm}^{-3}$; *b* $[\text{KMnO}_4]_0 = 0.08 \text{ mmol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 2 \text{ mmol dm}^{-3}$. Points as in Fig. 1

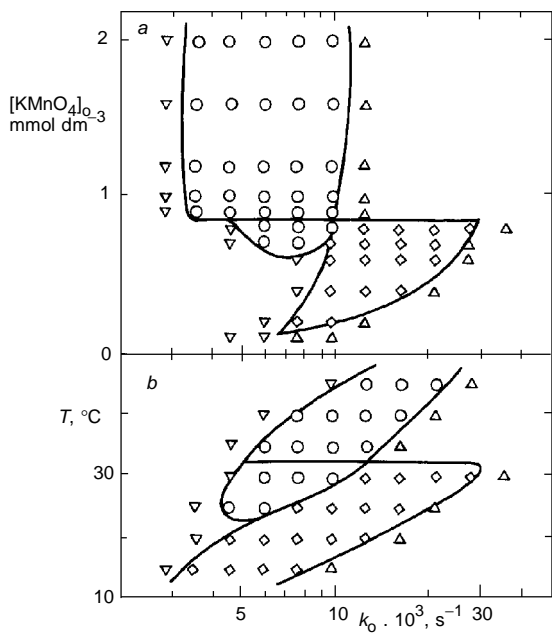


FIG. 5

Phase diagrams of the MnO_4^- - α -ketoglutaric acid (AKG) system in the planes: *a* $[\text{KMnO}_4]_0$ - k_0 , *b* temperature- k_0 . Fixed constraints: *a* $[\text{H}_3\text{PO}_4]_0 = 2 \text{ mmol dm}^{-3}$, $[\text{AKG}]_0 = 0.5 \text{ mmol dm}^{-3}$; *b* $[\text{KMnO}_4]_0 = 8 \text{ mmol dm}^{-3}$, $[\text{AKG}]_0 = 0.5 \text{ mmol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 2 \text{ mmol dm}^{-3}$. Points as in Figs 1 and 2

MnO_2 . The squares in the diagrams denote a steady state which is neither fully oxidized nor fully reduced, corresponds probably to Mn(IV) , and it is seen as the final state of damped oscillations with a value of $I = 7.5 \mu\text{A}$ at $k_0 = 9.1 \cdot 10^{-3} \text{ s}^{-1}$ (Fig. 3).

The permanganate oscillator with α -ketoglutaric acid has also quite a rich phenomenology. As Fig. 4 shows, while no region of damped oscillations is observed, a region of kinetic bistability occurs between the oscillatory state and the reduced steady state adjacent to the region of sustained oscillations. We have also been able to describe a "cross diagram" and so to find a region of sustained oscillations via kinetic bistability between the reduced and oxidized steady states. The sustained oscillations are promoted by relatively high concentrations of MnO_4^- ions and temperatures of the reaction system (Figs 5a, 5b). The phenomenon of kinetic bistability between the RSS and the oscillatory state is very sensitive to changes in the concentration of α -ketoglutaric acid (Fig. 6).

In principle, permanganate oscillators may involve all oxidation states of manganese between +7 and +2. Based on our experimental results we conclude, qualitatively at least, that MnO_2 colloids stabilized by H_2PO_4^- ions are reservoirs of solvated Mn(IV) ions which can interact with other species of manganese, particularly with Mn(II) :



yielding Mn(III) which is partly stabilized by chelation with keto dicarboxylic acid. The solvated Mn(IV) ions can also react with the substrate S (keto dicarboxylic acid):

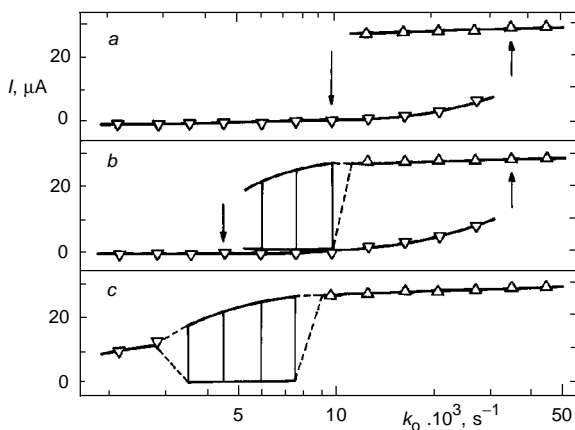
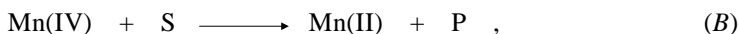


FIG. 6

Kinetic bistability at various concentrations of α -ketoglutaric acid (AKG). $[\text{KMnO}_4]_0 = 0.08 \text{ mmol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 2 \text{ mmol dm}^{-3}$, $[\text{AKG}]_0 = 0.6 \text{ mmol dm}^{-3}$ (a), 0.5 mmol dm^{-3} (b), 0.4 mmol dm^{-3} (c), temperature $30 \text{ }^\circ\text{C}$. Points as in Fig. 1



where P is a product of oxidation of the keto dicarboxylic acid. Reaction (B) is competitive with the oxidation of the substrate by MnO_4^- and by Mn(III), respectively.



Presumably, reaction (C) is no simple process; instead, it consists of two successive steps, the first of which – which is the rate-determining step – probably involves interaction of MnO_4^- ions with substrate molecules to produce species of manganese in the oxidation state 6 or 5. Very unstable in acidic solution, such species undergo a consecutive rapid disproportionation into Mn(VII) and Mn(IV).

Since the reduction of MnO_4^- ions by ketomalonic, oxalacetic, or α -ketoglutaric acid has an autocatalytic character¹, we assume that $k_C \ll k_B$ and $k_C \ll k_D$. If the MnO_4^- ions are in a stoichiometric excess over Mn^{2+} ions, the reaction



is also autocatalytic¹² and the rate constant k_E is relatively low. Mn^{2+} and MnO_4^- ions react only slowly with each other in acid solution containing no complexing agents which could serve as “conductors” of electrons.

The reaction steps (A) – (E) constitute a skeleton mechanism of the permanganate oscillators with keto dicarboxylic acids. Its mathematical simulation will be a next project of our laboratory after the values of the corresponding rate constants are available.

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